

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
2 May 2002 (02.05.2002)

PCT

(10) International Publication Number
WO 02/34869 A1

(51) International Patent Classification⁷: C11D 1/72

(21) International Application Number: PCT/EP01/12351

(22) International Filing Date: 18 October 2001 (18.10.2001)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
00309394.5 25 October 2000 (25.10.2000) EP

(71) Applicant (for AE, AG, AU, BB, BZ, CA, CY, GB, GD, GH, GM, IE, IL, KE, LC, LK, LS, MN, MW, NZ, SD, SG, SI, SZ, TT, TZ, UG, ZA, ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for AL, AM, AT, AZ, BA, BE, BF, BG, BJ, BR, BY, CF, CG, CH, CI, CM, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GA, GE, GN, GQ, GR, GW, HR, HU, ID, IS, IT, JP, KG, KP, KR, KZ, LR, LT, LU, LV, MA, MC, MD, MG, MK, ML, MR, MX, MZ, NE, NL, NO, PH, PL, PT, RO, RU, SE, SI, SK, SN, TD, TG, TJ, TM, TR, UA, UZ, VN, YU only): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN).

(72) Inventors: VAN DIJK, Marco, Franciscus; Unilever R & D Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT

Vlaardingen (NL). TOMLINSON, Alan, Digby; Lever Development Centre, Unilever Research Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).

(74) Agents: MULDER, Cornelis, Willem, Reinier et al.; Unilever PLC, Patent Department, Colworth House, Sharnbrook, Bedford, Bedfordshire MK44 1LQ (GB).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DISH-WASHING COMPOSITIONS

(57) Abstract: A machine dish wash composition comprising at least 4.0 wt% of an ethoxylated and/or propoxylated nonionic surfactant in which the nonionic surfactant has a cloud point in water of 14 or less. The invention also provides a method for washing articles in a dishwasher involving adding to the wash liquor a composition comprising an ethoxylated and/or propoxylated nonionic surfactant having a cloud point in water of 14 or less and treating the articles to be cleaned with the composition, wherein no additional rinse aid or salt are present in the dishwasher.

WO 02/34869 A1

- 1 -

DISH-WASHING COMPOSITIONS

The present invention is in the field of machine dishwashing. More specifically, the invention encompasses compositions for use in a machine dish wash formulation, which do not necessitate the addition of salt or rinse aid to the machine.

To wash articles in a commercially available dish washing machine usually entails using three product types. Salt is added to the salt compartment to soften the water, a dishwashing formulation is used to clean the articles, and a rinse aid is used to ensure that the articles are rinsed with no streaks or smears.

Consumers often find it inconvenient replace the salt and rinse aid in a dish wash machine.

WO 00/06684 (Benckiser) discloses a machine dish wash tablet. The tablet has a base composition that carries out it's function in the main wash cycle, and a separate core that acts as a rinse aid in the rinse cycle of the machine. However such a tablet is complicated to manufacture.

WO 95/07330 (Procter & Gamble) and US 5358655 (Henkel) describe dishwashing compositions in which certain well know nonionic surfactants are used..

- 2 -

The present invention relates to a composition for washing dishes that obviates the need for salt and rinse aid in the machine dishwashing process.

- 5 Accordingly, the present invention relates to a machine dish wash composition comprising at least 4.0 wt% of an ethoxylated and/or propoxylated nonionic surfactant in which the nonionic surfactant has a cloud point in water of 14 or less, preferably 12 or less.

10

Also described is a process for washing articles in a dishwasher comprising the steps of:

- i) adding a composition as described in the preceding
15 paragraph to the wash liquor of the dish washer followed by;

- ii) treating articles requiring cleaning with the wash
liquor in a conventional manner;

20

wherein no additional rinse aid is present within the dishwasher and no salt is present in the dishwasher to rejuvenate the ion exchange.

- 25 Also part of this inventive concept is a kit of parts comprising a composition as described above, and instructions stating that no rinse aid or salt is to be added to the dishwashing machine.

- 3 -

This invention also relates to the use of 4.0 wt% of an ethoxylated and/or propoxylated nonionic surfactant in which the nonionic surfactant has a cloud point in water of 12 or less in a dish washing composition, so that the composition
5 can be used in a dishwasher without a separate rinse aid composition (and ideally without separate salt) present in the machine.

Surfactant material

10

The surfactant system comprises ethoxylated and/or propoxylated nonionic surfactants, more preferably selected from nonionic ethoxylated/propoxylated fatty alcohol surfactants having a cloud point in water of 14°C or less,
15 preferably of 12°C or less, most preferably 10°C or less.

Examples of suitable nonionic surfactants having the required cloud points for use in the invention are found in the low- to non-foaming ethoxylated straight-chain alcohols
20 of the Plurafac® LF series, supplied by the BASF Company; Synperonic® RA series supplied by ICI Triton® DF series, supplied by the Rohm & Haas Company. A suitable nonionic surfactant is SLF 18 B 45, ex. Olin Chemicals. Suitable surfactants must however have the appropriate cloud point.

25

The ethoxylated and/or propoxylated nonionic surfactants are present at levels of at least 4.0 wt%, preferably 4-6 wt%, and in some instances more preferably 5 to 8 wt% of the total composition.

- 4 -

An anti-foam to suppress foaming is preferably present

If an anionic surfactant is used it is advantageously present at levels of 2 wt% or below.

5

Anti-scaling Agent

An anti-scaling agent is present in the composition as a preferred feature. It is preferable if the level

10 antiscaling agent is from 0.2 to 10 wt% of the total composition, preferably from 0.5 to 5 wt%.

Suitable anti-scaling agents include organic phosphonates, amino carboxylates, polyfunctionally-substituted compounds, and mixtures thereof.

15

Particularly preferred anti-scaling agents are organic phosphonates such as α -hydroxy-2 phenyl ethyl diphosphonate, ethylene diphosphonate, hydroxy 1,1-hexylidene, vinylidene 1,1 diphosphonate, 1,2 dihydroxyethane 1,1 diphosphonate and hydroxy-ethylene 1,1 diphosphonate. Most preferred is hydroxy-ethylene 1,1 diphosphonate (EDHP) and 2 phosphonobutane, 1,2,4 tricarboxylic acid (Bayhibit).

20

25 Also suitable are water soluble polymers prepared from an allyloxybenzenesulfonic acid monomer, a methallyl sulfonic acid monomer, a copolymerizable nonionic monomer and a copolymerizable olefinically unsaturated carboxylic acid monomer as described in US 5 547 612, or known as acrylic

- 5 -

5 sulphonated polymers as described in EP 851 022. Polymers of this type include polymers with as monomer units acrylic acid, methyl methacrylic acid, 4-sulfophenyl methylallyl ether and sodium methallyl sulfonate, such as Alcoperse 240 supplied by Alco. Also suitable is a terpolymer containing polyacrylate with 2-acrylamido-2-methylpropane sulfonic acid such as Acumer 3100 supplied by Rohm & Haas. It is preferable if polymers of this type have a molecular weight from 1,000 to 15,000, more preferably from 3,000 to 10,000.

10

As an alternative polymers and co-polymers of acrylic acid having a molecular weight between 500 and 20,000 can also be used, such as homo-polymeric polycarboxylic acid compounds with acrylic acid as the monomeric unit. The average weight of such homo-polymers in the acid form preferably ranges from 1,000 to 100,000, particularly from 3,000 to 10,000.

15

Also suitable are polymeric polycarboxylates are co-polymers derived from monomers of acrylic acid and maleic acid. The average molecular weight of these polymers in the acid form preferably ranges from 4,000 to 70,000.

20

A mixture of anti-scaling agents may be used, particularly useful are a mixture of organic phosphonates and a polymers having as monomer units acrylic acid, methyl methacrylic acid, 4-sulfophenyl methylallyl ether and sodium methallyl sulfonate,

25

- 6 -

Preferred ratios of antiscaling agent to nonionic surfactant are 1:3 to 3:1, more preferably 1:1 to 1:2

Builder Material

5

The compositions of the invention may contain a builder. The builder may be a phosphate or non-phosphate builder.

10 Compositions of the invention preferably comprise a water-soluble phosphate builder.

Phosphate builders are particularly preferred. Specific examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium
15 pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerisation ranges from about 6 to 21, and salts of phytic acid. Sodium or potassium tripolyphosphate is most preferred.

20 The level of builder is from 50 to 90% by weight, preferably from 55 to 80% by weight.

The compositions of the present invention may comprise a water-soluble nonphosphate builder. Suitable examples of
25 non-phosphorus-containing inorganic builders include water-soluble alkali metal carbonates, bicarbonates, sesquicarbonates, borates, silicates, including layered silicates such as SKS-6 ex. Clarent, metasilicates, and crystalline and amorphous aluminosilicates. Specific

- 7 -

examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates including layered silicates and zeolites.

5

Organic detergent builders can also be used as nonphosphate builders in the present invention. Examples of organic builders include alkali metal citrates, succinates, malonates, fatty acid sulfonates, fatty acid carboxylates,

10 nitrilotriacetates, oxydisuccinates, alkyl and alkenyl disuccinates, oxydiacetates, carboxymethyloxy succinates, ethylenediamine tetraacetates, tartrate monosuccinates, tartrate disuccinates, tartrate monoacetates, tartrate diacetates, oxidised starches, oxidised heteropolymeric
15 polysaccharides, polyhydroxysulfonates, polycarboxylates such as polyacrylates, polymaleates, polyacetates, polyhydroxyacrylates, polyacrylate/polymaleate and polyacrylate/ polymethacrylate copolymers, acrylate/maleate/vinyl alcohol terpolymers,

20 aminopolycarboxylates and polyacetal carboxylates, and polyaspartates and mixtures thereof. Such carboxylates are described in U.S. Patent Nos. 4,144,226, 4,146,495 and 4,686,062. Alkali metal citrates, nitrilotriacetates, oxydisuccinates, acrylate/maleate copolymers and
25 acrylate/maleate/vinyl alcohol terpolymers are especially preferred nonphosphate builders.

Silica

- 8 -

Silica material may be included in the composition.

Suitable forms of silica include amorphous silica, such as precipitated silica, pyrogenic silica and silica gels, such as hydrogels, xerogels and aerogels, or the pure crystal

5 forms quartz, tridymite or cristobalite, but the amorphous forms of silica are preferred. Suitable silicas may readily be obtained commercially. They are sold, for example under the Registered Trade Name Gasil 200 (ex Crosfield, UK).

10 Preferably, the silica is in the product in such a form that it can dissolve when added to the wash liquor. Therefore, addition of silica by way of addition anti-foam particles of silica and silicone oil is not preferred.

15 Therefore, it is preferred that silica material are used that have a particle size (as determined with a Malvern Laser, i.e. "aggregated" particles size) of at most 40 μ m, most preferably at most 20 μ m provides better results in the wash. In view of incorporation in a cleaning composition, it
20 is preferred that the particle size of the silica material is at least 1 μ m, more preferably at least 2 μ m, most preferably at least 5 μ m.

25 Preferably, the silica material is present in the cleaning composition at a level of at least 0.1%, more preferably at least 0.5%, most preferably at least 1% by weight of the cleaning composition and preferably at most 10%, more

- 9 -

preferably at most 8%, most preferably at most 5% by weight of the cleaning composition.

Silicates

5

The composition optionally comprises alkali metal silicates. When silicates are present, the SiO_2 level should be from 1% to 35%, preferably from 2% to 20%, more preferably from 3% to 10%, based on the weight of the ADD. The ratio of SiO_2 to the alkali metal oxide (M_2O , where M = alkali metal) is typically from 1 to 3.5, preferably from 1.6 to 3, more preferably from 2 to 2.8. Preferably, the alkali metal silicate is hydrous, having from 15% to 25% water, more preferably, from 17% to 20%.

15

The highly alkali metasilicates can in general be employed, although the less alkaline hydrous alkali metal silicates having a $\text{SiO}_2:\text{M}_2\text{O}$ ratio of from 2.0 to 2.4 are, as noted, greatly preferred. Anhydrous forms of the alkali metal silicates with a $\text{SiO}_2:\text{M}_2\text{O}$ ratio of 2.0 or more are also less preferred, because they tend to be significantly less soluble than the hydrous alkali metal silicates having the same ratio.

20

25 Sodium and potassium, and especially sodium, silicates are preferred. A particularly preferred alkali metal silicate is a granular hydrous sodium silicate having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of from 2.0 to 2.4 available from PQ Corporation, named Britesil H20 and Britesil H24. Most preferred is a

- 10 -

granular hydrous sodium silicate having a $\text{SiO}_2:\text{Na}_2\text{O}$ ratio of 2.0. While typical forms, i.e. powder and granular, of hydrous silicate particles are suitable, preferred silicate particles having a mean particle size between 300 and 900 microns and less than 40% smaller than 150 microns and less than 5% larger than 1700 microns.

Particularly preferred is a silicate particle with a mean particle size between 400 and 700 microns with less than 20% smaller than 150 microns and less than 1% larger than 1700 microns. Compositions of the present invention having a pH of 9 or less preferably will be substantially free of alkali metal silicate.

15 Enzymes

Enzymes may be present in the compositions of the invention. Examples of enzymes suitable for use in the cleaning compositions of this invention include lipases, peptidases, amylases (amylolytic enzymes) and others which degrade, alter or facilitate the degradation or alteration of biochemical soils and stains encountered in cleansing situations so as to remove more easily the soil or stain from the object being washed to make the soil or stain more removable in a subsequent cleansing step. Both degradation and alteration can improve soil removal.

Well-known and preferred examples of these enzymes are lipases, amylases and proteases. The enzymes most commonly

- 11 -

used in machine dishwashing compositions are amylolytic enzymes. Preferably, the composition of the invention also contains a proteolytic enzyme. Enzymes may be present in a weight percentage amount of from 0.2 to 7% by weight. For
5 amylolytic enzymes, the final composition will have amylolytic activity of from 10^2 to 10^6 Maltose units/kg. For proteolytic enzymes the final composition will have proteolytic enzyme activity of from 10^6 to 10^9 Glycine Units/kg.

10

Bleach Material

Bleach material is preferably incorporated in the composition.

15

The bleach material may be a chlorine- or bromine-releasing agent or a peroxygen compound. Peroxygen based bleach materials are however preferred.

20 Organic peroxy acids or the precursors therefor are typically utilized as the bleach material. The peroxyacids usable in the present invention are solid and, preferably, substantially water-insoluble compounds. By "substantially water-insoluble" is meant herein a water-solubility of less
25 than about 1% by weight at ambient temperature. In general, peroxyacids containing at least about 7 carbon atoms are sufficiently insoluble in water for use herein.

- 12 -

Inorganic peroxygen-generating compounds are also typically used as the bleaching material of the present invention. Examples of these materials are salts of monopersulphate, perborate monohydrate, perborate tetrahydrate, and
5 percarbonate.

Monoperoxy acids useful herein include alkyl peroxy acids and aryl peroxyacids such as peroxybenzoic acid and ring-substituted peroxybenzoic acids (e.g. peroxy-alpha-
10 naphthoic acid); aliphatic and substituted aliphatic monoperoxy acids (e.g. peroxy lauric acid and peroxy stearic acid); and phthaloyl amido peroxy caproic acid (PAP).

Typical diperoxy acids useful herein include alkyl diperoxy
15 acids and aryldiperoxy acids, such as 1,12-di-peroxy-dodecanedioic acid (DPDA); 1,9-diperoxyazelaic acid, diperoxybrassylic acid, diperoxysebacic acid and diperoxyisophthalic acid; and 2-decyldiperoxybutane-1,4-dioic acid.

20 Peroxyacid bleach precursors are well known in the art. As non-limiting examples can be named N,N,N',N'-tetraacetyl ethylene diamine (TAED), sodium nonanoyloxybenzene sulphonate (SNOBS), sodium benzoyloxybenzene sulphonate (SBOBS) and the cationic peroxyacid precursor (SPCC) as
25 described in US-A-4,751,015.

If desirably a bleach catalyst, such as the manganese complex, e.g. Mn-Me TACN, as described in EP-A-0458397, or the sulphonimines of US-A-5,041,232 and US-A-5,047,163, is to be incorporated, this may be presented in the form of a

- 13 -

second encapsulate separately from the bleach capsule or granule. Cobalt catalysts can also be used.

For peroxygen bleaching agents a suitable range is also from
5 0.5% to 3% avO (available Oxygen). Preferably, the amount of bleach material in the wash liquor is at least $12.5 \times 10^{-4}\%$ and at most 0.03% avO by weight of the liquor.

Anti-tarnishing Agents

10

Anti-tarnishing agents such as benzotriazole and those described in EP 723 577 (Unilever) may also be included.

Optional Ingredients

15

Optional ingredients are, for example, buffering agents, reducing agents, e.g., borates, alkali metal hydroxide and the well-known enzyme stabilisers such as the polyalcohols, e.g. glycerol and borax; crystal-growth inhibitors,
20 threshold agents; perfumes and dyestuffs and the like.

Reducing agents may e.g. be used to prevent the appearance of an enzyme-deactivating concentration of oxidant bleach compound. Suitable agents include reducing sulphur-oxy acids
25 and salts thereof. Most preferred for reasons of availability, low cost, and high performance are the alkali metal and ammonium salts of sulphuroxy acids including ammonium sulphite $((\text{NH}_4)_2\text{SO}_3)$, sodium sulphite (Na_2SO_3) , sodium bisulphite (NaHSO_3) , sodium metabisulphite $(\text{Na}_2\text{S}_2\text{O}_3)$,

- 14 -

potassium metabisulphite ($K_2S_2O_5$), lithium hydrosulphite ($Li_2S_2O_4$), etc., sodium sulphite being particularly preferred. Another useful reducing agent, though not particularly preferred for reasons of cost, is ascorbic acid. The amount of reducing agents to be used may vary from case to case depending on the type of bleach and the form it is in, but normally a range of about 0.01% to about 1.0% by weight, preferably from about 0.02% to about 0.5% by weight, will be sufficient.

Compositions according to the invention are preferably processed to be in the form of a tablet, although in some embodiments other product forms (e.g. as a powder) may be contemplated and preferred.

pH of wash liquor

The invention relates to washing processes in mechanical dish washing machines wherein the wash liquor has a low pH. By "low pH" is meant here that the pH of the wash liquor is preferably higher than about 6.5, more preferably 7.5 or higher, most preferably 8.5 or higher. Preferably the pH is lower than about 11, more preferably lower than about 10.5, more preferably lower than about 9.5. The most advantageous pH range is from 8.5 to 10.5.

The invention will now be illustrated by the following non-limiting Examples.

- 15 -

All percentages are on a weight basis.

Table 1

	Example A	Example B
Na Tripolyphosphate	60.60	60.60
PA25 CL ¹	3.30	3.30
Na Disilicate -	11.8	7.8
Na Perborate Monohydrate	15.00	15.00
TAED (83%)	2.50	2.50
Na EHDP Granular - Monsanto SPE 9528	1.10	1.10
T-Blend Savinate TXT/Termamyl 5.4/33	3.05	3.05
Nonionic ²	1.00	5.00
Minors	to 100.00	to 100.00

5

- 1) acrylic acid polymer ex BASF
- 2) Nonionic surfactant, ex BASF (LF 403)

10

Spot formation on glassware is a primary reason why rinse aids are added to dish washing machines. It has been found that the contact angles on glass correlate very well with spot scores on glasses. Experiments having low spot scores (that is few deposits on glasses, so better results) were found when contact angles were also low (less than 20).

15

- 16 -

8 glass plates were subjected to the following treatment to simulate their washing in the dish washer. They were placed in a rack which was placed in a beaker containing 5 litres of water (40 FH) at 60°C, 30g of composition to be tested and 3g of egg yolk. The plates were kept in this stirred solution for 45 minutes at 60°C (main wash simulation). The plates were removed from the solution and placed in a beaker containing 5 litre of water at 60°C with 15ml of the original solution (this simulates carry over in the rinse cycle, rinse simulation) for 5 minutes. The plates were removed and their contact angle with the rinse solution was measured using a Contact angle Goniometer model A-1 00.

Various treatments were used:

15

Experiment conducted with Example 1 in the main wash simulation, the rinse simulation and used to measure the contact angle - **Treatment 1**

20

Experiment conducted with Example A in the main wash simulation, the rinse simulation and used to measure the contact angle - **Treatment A**

25

To demonstrate that the contact angle was influenced by the washing process and not merely the rinse solutions used to measure the contact angles, plates were placed in 60°C water with no added product for 60 minutes. The contact angle in the rinse solution was measured.

30

Experiment conducted with water in the main wash simulation and the rinse simulation, Example 1 diluted as for rinsing

- 17 -

procedure (30g in 5 litres of water, diluted by taking 15 ml of this solution and adding to a further 5 litres of water) used to measure the contact angle - **Treatment B**

- 5 Experiment conducted with water in the main wash simulation and the rinse simulation, Example A diluted as for rinsing procedure (30g in 5 litres of water, diluted by taking 15 ml of this solution and adding to a further 5 litres of water) used to measure the contact angle - **Treatment C**

10

The results are as follows:

Contact angle(average)	
Treatment 1	8
15 Treatment A	27
Treatment B	28
Treatment C	33.

- 18 -

CLAIMS

1. A process for washing articles in a dishwasher
comprising the steps of:
 - 5 i) adding a composition comprising at least 4% by weight
of an ethoxylated and/or propoxylated nonionic
surfactant which has a cloud point in water of 14 or
less to the wash liquor of the dish washer followed by;
 - 10 ii) treating articles requiring cleaning with the wash
liquor in a conventional manner;
wherein no additional rinse aid is present within the
dishwasher.
- 15 2. A process according to claim 1 wherein no salt is added
to the dishwasher to rejuvenate the ion exchange.
- 20 3. A process according to claim 1 or claim 2 in which the
level of nonionic surfactant is from 4% to 8%,
preferably from 5% to 8 wt% of the total composition.
- 25 4. A process according to any of the preceding claims in
which the nonionic surfactant is selected from nonionic
surfactants having a cloud point in water of 12 or
less.
5. A process according to any of the preceding claims,
which further comprises an anti-scaling agent in the
composition.

- 19 -

6. A process according to claims 5 in which the level of antiscaling agent in the composition is from 0.5 to 5 wt%.
- 5 7. A process according to any of the preceding claims wherein the composition comprises greater than 50 wt% of a builder.
8. A process according to claim 7 in which the builder is
10 a water-soluble phosphate.
9. A process according to any of the preceding claims in which the composition is in the form of a tablet.
- 15 10. A machine dish wash composition comprising at least 4.0 wt% of an ethoxylated or propoxylated nonionic surfactant in which the nonionic surfactant has a cloud point in water of 14 or less, the composition being provided together with instructions not to include a
20 rinse aid in the machine dishwashing process.
11. A machine dishwashing composition according to claim 10 provided together with instructions not to include salt in the machine dishwashing process.
25
12. A machine dish wash composition according to claim 10 or claim 11 in which the level of nonionic surfactant is from 4% to 8%, preferably 5% to 8 wt% of the total composition.

- 20 -

13. A machine dish wash composition according to any one of
claims 11 to 13 in which the nonionic surfactant is
selected from nonionic surfactants having a cloud point
5 in water of 12 or less.

14. A machine dish wash composition according to any one of
claims 10 to 13, which further comprises an anti-
scaling agent.

15. A machine dish wash composition according to claim 14
in which the level of antiscaling agent is from 0.5 to
5 wt%.

16. A machine dish wash composition according to any one co
claims 10 to 15 comprising greater than 50wt% of a
builder.

17. A machine dish wash composition according to claim 16
in which the builder is a water-soluble phosphate.

18. A machine dish wash composition according to any one of
claims 10 to 17 in which the composition is in the form
of a tablet.

19. A kit of parts comprising:

(i) a composition as claimed in any one of claims
10 to 18 and;

- 21 -

- (ii) instructions stating that no rinse aid or salt is to be added to the dishwashing machine

20. Use of at least 4.0 wt% of an ethoxylated and/or
5 propoxylated nonionic surfactant in which the nonionic
surfactant has a cloud point in water of 14 or less in
a dish washing composition so that the composition can
be used in a dishwasher without a separate rinse aid
composition being present in the machine.

10
21. Use according to claim 20 wherein the composition can
be used in a dishwasher without separate salt being
present in the machine.

INTERNATIONAL SEARCH REPORT

 Inte I Application No
 PCT/EP 01/12351

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C11D1/72

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D A47L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 32823 A (ECOLAB INC) 30 July 1998 (1998-07-30)	1,4-6, 10, 13-15, 19,20
A	page 12, line 19 -page 13, line 6 page 17, line 12 - line 30; claim 1; example 2	3,7-9, 12,16-18
X	US 4 123 375 A (ALTENSCHOPFER THEODOR ET AL) 31 October 1978 (1978-10-31) abstract; examples 1,3 ----- -/--	1,3,7,8, 10,12, 16,17, 19,20

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *B* document member of the same patent family

Date of the actual completion of the international search

18 February 2002

Date of mailing of the international search report

27/02/2002

Name and mailing address of the ISA

 European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax: (+31-70) 340-3016

Authorized officer

Saunders, T

INTERNATIONAL SEARCH REPORT

Int Application No
PCT/EP 01/12351

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 306 987 A (KANEKO THOMAS M) 22 December 1981 (1981-12-22)	1,3,4,7, 8,10,12, 13,16, 17,19 20
A	abstract; claims 1,2; example 1 ---	
X	WO 96 37596 A (HENKEL KGAA) 28 November 1996 (1996-11-28)	10, 12-16, 18,19
A	page 7, paragraph 4; examples 3,4,17-20 ---	1,3-9, 17,20
X	US 5 358 655 A (JACOBS JOCHEN ET AL) 25 October 1994 (1994-10-25) cited in the application	10,12, 13,16, 18,19
A	example 2A ---	1,3-7,9, 14,15,20
X	WO 95 07330 A (PROCTER & GAMBLE) 16 March 1995 (1995-03-16) cited in the application	10, 12-15,19
A	example V ---	1,3-8, 16,17,20
X	WO 92 17565 A (HENKEL KGAA) 15 October 1992 (1992-10-15)	10, 12-14, 16,19
A	page 10 ---	1,3-7, 15,20
X	WO 99 41349 A (AGENCY DESIGN SERVICES LIMITED (GB)) 19 August 1999 (1999-08-19)	10,12, 13,19
A	abstract; examples 2A,2B,4 ---	1,3,4,7, 16,20
X	WO 00 46329 A (UNILEVER PLC) 10 August 2000 (2000-08-10)	10,19
A	abstract; tables 1-3 ---	1-7, 12-16, 20,21
X	EP 0 308 221 A (ROHM & HAAS) 22 March 1989 (1989-03-22)	10,14,19
A	table 1 ---	1,3-7, 12,13, 15,16,20
X	WO 98 11185 A (PROCTER & GAMBLE) 19 March 1998 (1998-03-19)	10, 12-14, 16-19
A	claim 1; example 3V ---	1,3-9, 15,20
	--- -/--	

INTERNATIONAL SEARCH REPORT

In Application No
PCT/EP 01/12351

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 00 06684 A (BENCKISER N.V.) 10 February 2000 (2000-02-10) cited in the application claim 1; examples 1A,5,7; table 1 ---	1,3-10, 12-20
A	WO 98 11187 A (PROCTER & GAMBLE) 19 March 1998 (1998-03-19) page 7, line 35 -page 8, line 37; example 14 ---	1,3-10, 12-20
A	EP 1 026 230 A (UNILEVER) 9 August 2000 (2000-08-09) claims 1,3,21; example I -----	1-10, 12-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int Application No

PCT/EP 01/12351

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9832823	A	30-07-1998	US 5876514 A AU 740960 B2 AU 5238498 A BR 9714652 A CN 1245524 A EP 0956331 A1 JP 2001505614 T TW 404980 B WO 9832823 A1 ZA 9709936 A	02-03-1999 15-11-2001 18-08-1998 03-10-2000 23-02-2000 17-11-1999 24-04-2001 11-09-2000 30-07-1998 05-05-1999
US 4123375	A	31-10-1978	DE 2552506 A1 AT 359177 B AT 860776 A BE 848533 A1 BR 7607745 A CA 1066982 A1 CH 624427 A5 FR 2332320 A1 IT 1069881 B NL 7612101 A	26-05-1977 27-10-1980 15-03-1980 20-05-1977 04-10-1977 27-11-1979 31-07-1981 17-06-1977 25-03-1985 24-05-1977
US 4306987	A	22-12-1981	NONE	
WO 9637596	A	28-11-1996	DE 19518693 A1 WO 9637596 A1	28-11-1996 28-11-1996
US 5358655	A	25-10-1994	DE 4112075 A1 AT 123804 T DE 59202554 D1 DK 579659 T3 WO 9218604 A1 EP 0579659 A1 ES 2073295 T3 JP 3147901 B2 JP 6506493 T	15-10-1992 15-06-1995 20-07-1995 06-11-1995 29-10-1992 26-01-1994 01-08-1995 19-03-2001 21-07-1994
WO 9507330	A	16-03-1995	AT 164622 T DE 69409391 D1 DE 69409391 T2 EP 0717766 A1 ES 2114218 T3 WO 9507330 A1 US 5698046 A	15-04-1998 07-05-1998 29-10-1998 26-06-1996 16-05-1998 16-03-1995 16-12-1997
WO 9217565	A	15-10-1992	DE 4110510 A1 WO 9217565 A1 EP 0578659 A1	01-10-1992 15-10-1992 19-01-1994
WO 9941349	A	19-08-1999	AU 2527299 A WO 9941349 A1 GB 2339205 A	30-08-1999 19-08-1999 19-01-2000
WO 0046329	A	10-08-2000	GB 2346319 A AU 2110500 A BR 0008014 A WO 0046329 A1 EP 1149144 A1	09-08-2000 25-08-2000 20-11-2001 10-08-2000 31-10-2001

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int : Application No

PCT/EP 01/12351

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0046329	A	AU 2293500 A	25-08-2000
		WO 0046341 A1	10-08-2000
		EP 1026230 A1	09-08-2000
		FR 2789291 A1	11-08-2000
		IT T020000024 U1	06-08-2001
		PT 102413 A	31-08-2000
EP 0308221	A 22-03-1989	AU 2231488 A	23-03-1989
		CA 1314187 A1	09-03-1993
		DE 3870560 D1	04-06-1992
		EP 0308221 A1	22-03-1989
		JP 1158098 A	21-06-1989
		NO 884074 A ,B,	20-03-1989
		ZA 8806913 A	30-05-1989
WO 9811185	A 19-03-1998	GB 2327948 A	10-02-1999
		AU 4263897 A	02-04-1998
		BR 9712817 A	23-11-1999
		EP 0925341 A1	30-06-1999
		JP 2000502750 T	07-03-2000
		TR 9901131 T2	21-07-1999
		WO 9811185 A1	19-03-1998
		AU 4412697 A	02-04-1998
		BR 9712813 A	23-11-1999
		EP 0927237 A1	07-07-1999
		WO 9811187 A1	19-03-1998
		US 6034044 A	07-03-2000
		US 5877134 A	02-03-1999
		US 6013613 A	11-01-2000
WO 0006684	A 10-02-2000	DE 19834180 A1	03-02-2000
		AU 5163599 A	21-02-2000
		WO 0006684 A1	10-02-2000
		EP 1100862 A1	23-05-2001
WO 9811187	A 19-03-1998	AU 4263897 A	02-04-1998
		AU 4412697 A	02-04-1998
		BR 9712813 A	23-11-1999
		BR 9712817 A	23-11-1999
		EP 0925341 A1	30-06-1999
		EP 0927237 A1	07-07-1999
		JP 2000502750 T	07-03-2000
		TR 9901131 T2	21-07-1999
		WO 9811185 A1	19-03-1998
		WO 9811187 A1	19-03-1998
		US 6034044 A	07-03-2000
		US 5877134 A	02-03-1999
		US 6013613 A	11-01-2000
EP 1026230	A 09-08-2000	GB 2346319 A	09-08-2000
		AU 2110500 A	25-08-2000
		AU 2293500 A	25-08-2000
		BR 0008014 A	20-11-2001
		WO 0046329 A1	10-08-2000
		WO 0046341 A1	10-08-2000
		EP 1026230 A1	09-08-2000
		EP 1149144 A1	31-10-2001
		FR 2789291 A1	11-08-2000

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Application No

PCT/EP 01/12351

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1026230	A	IT T020000024 U1 PT 102413 A	06-08-2001 31-08-2000